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Mechanisms of Selenate Adsorption on Iron Oxides and Hydroxides

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Selenium is a naturally occurring element which naturally occurs in rocks and soil and can also be released by manufacturing processes. In the environment, selenium combines with oxygen to form many different molecules, such as selenate (SeO_4^{2-}), which is known to bind to ferric oxides and hydroxides. Because of selenate's toxicity to animals and its mobility in the soil, the mechanism of selenate adsorption on iron oxides has been the subject of intense debate. Researchers from the University of Delaware in Newark have determined selenate bonding mechanisms on hematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), and amorphous iron hydroxide ($\text{Fe}(\text{OH})_3$).

Selenate (SeO_4^{2-}) is the fully oxidized form of selenium, an essential micronutrient for plant growth. When soil selenate levels are high, it often accumulates in plants and can then prove toxic to animals that ingest this vegetation. Alternatively, deficiency symptoms are commonly seen in animals when selenium levels in plants are low. So, understanding the chemistry of selenate in soils is important for minimizing potentially hazardous environmental effects on animal populations.

In soils and sediments, selenate preferentially reacts with ferric [Fe(III)] oxides and hydroxides. However, the mechanism of selenate binding on iron oxides has been the subject of intense debate. Some researchers have proposed that the bonding is electrostatic and weak, while others have proposed that covalent chemical bonds form between selenate and iron oxides. The nature of bonding can have a large effect on the transport and availability of selenate in the environment, so, we decided to investigate this adsorption mechanism when selenate binds to hematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), and

amorphous iron hydroxide ($\text{Fe}(\text{OH})_3$).

The objectives of our work were to determine the effects of pH (the concentration of protons in solution), surface loading, and ionic strength (an average of the concentrations of the ions present) on selenate adsorption mechanisms. Hematite, goethite, and amorphous iron hydroxide were chosen due to their important differences in structure and their common occurrence in soils.

Extended x-ray absorption fine structure (EXAFS) was the primary spectroscopic tool chosen due to its suitability to determine local bonding environments of selenate on all

three sorbents. EXAFS spectra were collected at the selenium K-edge at beam line X11A of the National Synchrotron Light Source at Brookhaven National Laboratory. Additional information about selenate adsorption mechanisms on hematite was obtained using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy.

Selenate forms different surface complexes on iron oxides, depending upon pH, ionic strength, and iron oxide structure. On hematite, we noticed that selenate ions directly interact with iron, with no intermediate water molecules present, a structure called inner-sphere complex. Also, the adsorbed selenate ions form single covalent bonds (formed by sharing electrons) with the surface, a process known as monodentate. These inner-sphere monodentate complexes were observed at all pH and ionic strength values considered in the study.

On goethite and amorphous iron hydroxide, we noticed that selenate forms outer-sphere complexes, in which a water molecule is positioned between each selenate



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and iron atom, at pH values of 6 (slightly acidic) and above (alkaline). For pH values between 3.5 and 6 (acidic), we noticed a mixture of outer- and inner-sphere monodentate complexes. ATR-FTIR spectroscopy also suggests that some hydrogen bonding is present in this inner-sphere complex.

The EXAFS spectra are shown for aqueous selenate (pH 4) and selenate adsorbed on goethite at pH values of 6 and 3.5 in **figure 1**. A

schematic representation of the outer- and inner-sphere monodentate complexes is provided in **figure 2**.

This study and others have shown that outer-sphere and inner-sphere complexation often occur simultaneously. We noticed that changes in the relative importance of different surface complexes depend on the pH and ionic strength of the solution containing the sorbent, as well as on the nature of the sor-

bent. So, to adequately characterize selenate reactivity at the molecular level, we consider it is necessary to conduct EXAFS studies over a wide range of reaction conditions and with a range of minerals. Such studies are expected to produce a far clearer picture of how selenate, and oxyanions in general, reacts under constantly changing conditions in the natural world.

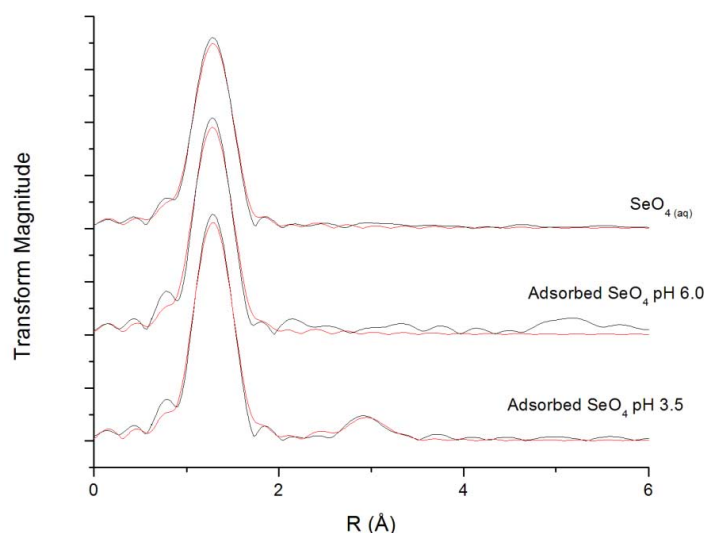


Figure 1. (part b) Selenium K-edge extended x-ray absorption fine structure (EXAFS) spectra of aqueous selenate, selenate adsorbed on goethite at pH = 6.0 (outer-sphere surface complex), and selenate adsorbed on goethite at pH = 3.5 (inner-sphere surface complex).

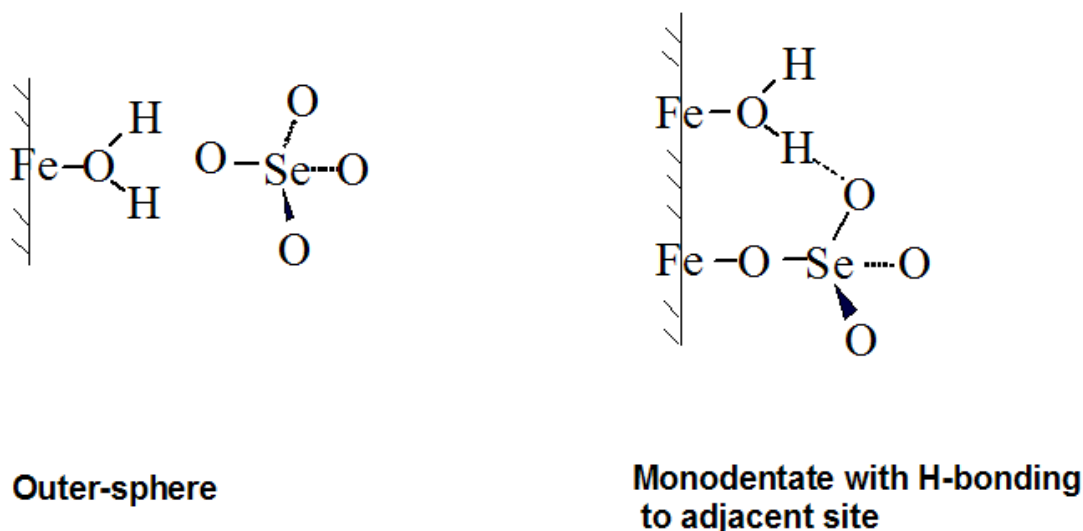


Figure 2. Bonding of selenate on goethite derived from EXAFS and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. (A) Outer-sphere complex (water molecule positioned between selenate and the iron atom); (B) Inner-sphere (no water molecule is positioned between selenate and the iron atom) and monodentate (shared electrons between selenate and the iron atom) complex.